# (19) World Intellectual Property Organization International Bureau





### (43) International Publication Date 15 November 2001 (15.11.2001)

#### **PCT**

# (10) International Publication Number WO 01/85895 A1

(51) International Patent Classification7: C11D 17/00, A61K 7/50

(21) International Application Number: PCT/EP01/04937

(22) International Filing Date: 1 May 2001 (01.05.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

00201710.1 12 May 2000 (12.05.2000) EP 01200361.2 1 February 2001 (01.02.2001) EP

(71) Applicant (for AE, AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, FR, GA, GE, GN, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LC, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, NE, NL, NO, PL, PT, RO, RU, SE, SI, SK, SN, TD, TG, TJ, TM, TR, UA, UZ, VN, YU only): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LK, LS, MN, MW, MZ, NZ, SD, SG, SL, SZ, TT, TZ, UG, ZA, ZW only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London, Greater London EC4P 4BQ (GB).

(71) Applicant (for IN only): HINDUSTAN LEVER LTD [IN/IN]; Hindustan Lever House, 165-166 Backbay Reclamation, 400 020 Mumbai (IN). (72) Inventors: BOLZONI, Giuseppe, Vincenzo; Lever Faberge Italia, Via Lever Gibbs 3, 1-26841 Casalpusterlengo (IT). LODOLA, Rita; Lever Faberge Italia, via Lever Gibbs 3, I-26841 Casalpusterlengo (IT). PUERARI, Francesco, Maria; Lever Faberge Italia, via Lever Gibbs 3, I-26841 Casalpusterlengo (IT). VALCARENGHI, Ivan; Lever Faberge Italia, via Lever Gibbs 3, I-26841 Casalpusterlengo (IT).

(74) Agent: ROSEN JACOBSON, Frans; Unilever Patent Department, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

#### Published:

with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

/85895 A1

(54) Title: UNIT DOSE CLEANING PRODUCT

(57) Abstract: The invention concerns unit dose cleaning products, which are completely soluble in water, contain a detergent, are rigid and have a smooth surface. The products are at least partly translucent or transparent. Preferably the product has a rigid outer shell and liquid core.

#### Unit dose cleaning product

## 5 Field of the invention

The invention relates to firm, water soluble unit dose cleaning products.

10

## Background of the invention

Cleaning products are traditionally often liquids, viscous or thin, such as known for personal cleaning (bath and shower

15 liquids and shampoos) or for domestic cleaning (hand dish wash and other hard surface cleaning, laundry-cleaning etc.) Other products are solids, such as powders, granules, small capsules (up to 2mm diameter) or more recently tablets, for laundry and machine dish wash, and soap bars for skin cleaning. Recently,

20 so called unit dose products are experiencing an increasing success with consumers, because they eliminate the need for manipulating, and possibly spilling, liquids or powders and simplify the use of a correct dose of the cleaning product for the required purpose. Examples thereof are the laundry and

25 machine dish wash tablets mentioned above and recently described in F.Schambil and M. Böcker, Tenside Surf. Det. 37 (2000) 1.

Such tablets have the disadvantage that they may crumble or 30 break during transport or handling, which will still cause spillage of the cleaning product. Also, unpacking and dosing of the tablets will require the consumer to have direct skin contact with the product, which he may feel uncomfortable with

because of fear that the product is aggressive to the skin. Furthermore, tablets, which consist of compressed powders and are clearly recognisable as such, are rather unsightly, unpleasant to the touch and do not give the impression of a 5 technologically advanced product. Some of these disadvantages may be overcome by providing a water-soluble coating, such as described in EP-A-0 716 144. However, such products remain recognisable as consisting primarily of a compressed powder. The look and feel of such tablets, whether or not coated, 10 provide no assurance to the consumer that the product will completely dissolve in use and be disappeared after use and will not leave any unsightly remains in the form of powder patches on cleaned laundry or in the bowl or bucket used for cleaning a floor or other hard surface, or in the form of 15 streaks and stripes on the clean floor, table top or dishes or other surface cleaned with the product.

Many of the disadvantages mentioned above would be absent with a unit dose liquid product and indeed such products are known as sachets and the like. However, these have the disadvantage that a packaging of liquid has to be opened, sometimes leading to spilling or other messy situations, and that the packaging with remains of the liquid has to be disposed of.

25 This problem has been met with round capsules made of gelatin or other soft wall material and filled with a liquid cleaning composition. They are best known for bath use, such as e.g. described in US 3,705,102, US 4,597,885, EP-A-0 261 754, WO 96/24328 and EP-A-0 573 978. Similar capsules have also been proposed for laundry cleaning products in EP-A-0 339 707 and for dish wash products in WO94/14941 and EP-A-0 879 874. These capsules have the advantage that they can simply be added to a bath, bucket or bowl with hot water in which they dissolve to

3

produce a cleaning solution. However, they are not very appealing to the consumer in that they are generally rather soft and squeezy and thereby convey to the consumer the message that they are not very strong and may be susceptible to leakage if not handled carefully. Also they have a rather dull appearance and it is impossible for the consumer to have a clue of what is inside. Furthermore, their origin as a bath product does not convey the message of a strong and modern cleaning product for use for e.g. laundry or hard surface cleaning.

10

Therefore, there is a need for a unit dose cleaning product which is agreeable to the touch, looks appealing to the consumer and provides him/her with a clue of its contents.

15

## Brief description of the invention

It is an object of the present invention to provide a rigid unit dose cleaning product which dissolves easily and 20 completely in an amount of water conventionally used for a household cleaning operation and which has an attractive shape.

It is a further object of the invention to provide a unit dose cleaning product with a smooth surface.

25

30

It is another object of the invention to provide a unit dose cleaning product which is at least partly transparent or translucent so as to enable the consumer to obtain a visual clue of the contents of the product.

## Detailed description of the invention

All percentages mentioned herein are by weight, calculated on the total product, unless specifically indicated otherwise.

For the purposes of this invention a unit dose cleaning product is defined as a product of which a limited number of units provide the right amount of detergent to perform the cleaning operation for which the product is intended. This limited

10 number will normally be between 1 and 10, preferably not more than 5 and typically between 1 and 3. Thus, for a floor cleaning product these 1-3 units in a bucket of water will usually provide a cleaning liquid of the desired strength, whereas for a hand dishwash product the equivalent would be 1-3 units in a dishwash bowl.

The unit dose cleaning product is water soluble to the extent that the dose (i.e. number of units) intended for a given amount of water should be able to give a clear solution and no solid particles visible to the naked eye should remain. A suitable dose unit should quickly dissolve 2000 times its weight of water, which amounts to a dilution of 2000 fold. Thus, all components in 10g of unit dose product should be completely soluble in 201 of water. More suitably the product, and therefore all the components in it, would also allow a dilution of only 1000 times, more preferably only 500 times, even more preferably 200 times. Such solutions may be made in hot water, i.e. 100°C or below, but preferably the product is also completely soluble in less hot water, i.e. at 70°C or below, more preferably at 50°C or even 30°C. Quick dissolution is defined as complete dissolution within 5 minutes (with

slight stirring if desired), preferably within 2 minutes, more preferably within 1 minute

Suitable unit dose products meeting these requirements, as well as being easy to handle, generally have a minimum dimension in any one direction of at least 2mm and preferably at least 5mm, more preferably at least 10mm, whereas the maximum dimension in any one direction should generally not exceed 100mm, preferably be at most 60mm, more preferably at most 40mm. The volume of the unit dose is generally between 0.5ml and 20ml, preferably below 10ml, more preferably 1-5ml.

The property of being smooth and agreeable to the touch means that at least the majority of the surfaces of the product

15 according to the invention do not present the porous, powdery or grainy surface structure which is well known of tablets made of a compressed powder or granular material.

The unit dose products according to the invention are not soft or squeezy, as is known from capsules having a wall made of gelatin or similar material, and are therefore called "rigid". This does not necessarily mean that it is hard and completely inflexible, because this may lead to brittleness and cause the products to be susceptible to breaking. However, it does mean that the unit dose product cannot be squeezed by normal hand pressure such that its dimensions in any one direction alter by more than 10% of the original value, preferably not more than 5%, more preferably not more than 2% or even 1%. Of course, exerting extreme pressure may cause the product to break. Also the products according to the invention cannot be compressed by more than 10% without breaking, preferably not more than 5%, more preferably not more than 2% or even 1%.

The unit dose products according to the invention may be substantially homogeneous, in which case the bulk of a unit consists of a solid and homogeneous mixture comprising a solid 5 structuring material, one or more detergent surfactants and optionally other benefit agents suitable for the intended use of the product. The structuring material is easily soluble as outlined above, but not hygroscopic. The product may contain discrete solid particles of one or more of the components as long as these do not interfere with complete dissolution and therefore do not remain as such in the ready to use cleaning

Suitable structuring materials comprise synthetic or natural polymers such as starch derivatives (e.g. chemically modified starches), polyvinyl alcohol, polyvinylpyrrolidone, polyethylene glycol or polyethylene/polypropylene glycol, or mono-, di- or oligosaccharides such as sorbitol, maltitol, isomalt, glucose, saccharose or mixtures thereof. Preferred structuring materials are those which can be converted into a viscous liquid or "molten glass"-like state on heating while reverting to a solid glassy state on cooling to room temperature.

solution.

25 Alternatively, and preferably, the product may have a rigid outer shell comprising the structuring material, such as mentioned above, which surrounds a solid or liquid core comprising detergent surfactant. If the core is solid, it may have a composition which is substantially similar to the composition of the homogeneous product above, be it that in general less structuring material and more detergent surfactant and other benefit agents will be present. The shell will preferably consist for the major part, or even entirely, of

WO 01/85895

PCT/EP01/04937

structuring material. However, in addition to this, it may contain a disintegrant as outlined below.

7

In a further preferred embodiment the core comprises a liquid.

5 This liquid may be anything from thin to very viscous or gellike. Alternatively it may be absorbed in a sponge-like solid structure. As outlined above for the total product, the core will dissolve quickly and easily into the amount of water for which it is intended without leaving any solid or gel particles 10 visible to the naked eye.

The surfactants may be chosen from anionic, cationic, nonionic, zwitterionic or amphoteric surfactants known in the art and any suitable mixture thereof.

15

25

A suitable class of anionic surfactants are water-soluble salts of organic sulphuric acid esters and sulphonic acids having in the molecular structure an alkyl group containing 8-22 C atoms or an alkylaryl group containing 6-20 C atoms in the alkyl part.

Examples of such anionic surfactants are water soluble salts of:

- long chain (i.e. 8-22 C-atom) alcohol sulphates (hereinafter referred to as PAS), especially those obtained by sulphating the fatty alcohols produced by reducing the glycerides of tallow or coconut oil;
- alkylbenzene-sulphonates, such as those in which the alkyl group contains from 6 to 20 carbon atoms;
- secondary alkanesulphonates.
- 30 Also suitable are the salts of:
  - alkylglyceryl ether sulphates, especially of the ethers of fatty alcohols derived from tallow and coconut oil;

8

- fatty acid monoglyceride sulphates;
- sulphates of ethoxylated aliphatic alcohols containing 1-8 ethyleneoxy groups;
- alkylphenol ethyleneoxy-ether sulphates with from 1 to 8
   ethyleneoxy units per molecule and in which the alkyl groups contain from 4 to 14 carbon atoms;
  - the reaction product of fatty acids esterified with isethionic acid and neutralised with alkali.
- 10 A suitable class of nonionic surfactants can be broadly described as compounds produced by the condensation of simple alkylene oxides, which are hydrophilic in nature, with an organic hydrophobic compound which may be aliphatic or alkylaromatic in nature. The length of the hydrophilic or
- 15 polyoxyalkylene chain which is attached to any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired balance between hydrophilic and hydrophobic elements. This enables the choice of nonionic surfactants with the right HLB. Particular examples include:
- 20 the condensation products of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut alcohol ethylene oxide condensates having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol;
- 25 condensates of alkylphenols having C6-C15 alkyl groups with 5 to 25 moles of ethylene oxide per mole of alkylphenol;
  - condensates of the reaction product of ethylene-diamine and propylene oxide with ethylene oxide, the condensates containing from 40 to 80% of ethyleneoxy groups by weight and having a molecular weight of from 5,000 to 11,000.

30

WO 01/85895

Other classes of nonionic surfactants are:

- alkylglycosides, which are condensation products of long chain aliphatic alcohols and saccharides;
- tertiary amine oxides of structure RRRNO, where one R is an alkyl group of 8 to 20 carbon atoms and the other R's are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, e.g. dimethyldodecylamine oxide;
  - tertiary phosphine oxides of structure RRRPO, where one R is an alkyl group of 8 to 20 carbon atoms and the other R's are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine oxide;
  - dialkyl sulphoxides of structure RRSO where one R is an alkyl group of from 10 to 18 carbon atoms and the other is methyl or ethyl, for instance methyl-tetradecyl sulphoxide;
- 15 fatty acid alkylolamides;
  - alkylene oxide condensates of fatty acid alkylolamides;
  - alkyl mercaptans.

Suitable amphoteric surfactants are derivatives of aliphatic

20 secondary and tertiary amines containing an alkyl group of 8 to

20 carbon atoms and an aliphatic group substituted by an anionic

water-solubilising group, for instance sodium 3-dodecylamino
propionate, sodium 3-dodecylaminopropane-sulphonate and sodium

N-2-hydroxy-dodecyl-N-methyltaurate.

25

10

Examples of suitable cationic surfactants can be found among quaternary ammonium salts having one or two alkyl or aralkyl groups of from 8 to 20 carbon atoms and two or three small aliphatic (e.g. methyl) groups, for instance

30 cetyltrimethylammonium bromide.

10

Examples of suitable zwitterionic surfactants can be found among derivatives of aliphatic quaternary ammonium, sulphonium and phosphonium compounds having an aliphatic group of from 8 to 18 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance 3-(N,N-dimethyl-N-hexadecylammonium)-propane-1-sulphonate betaine, 3-(dodecylmethyl-sulphonium)-propane-1-sulphonate betaine and 3-(cetylmethyl-phosphonium)-ethanesulphonate betaine.

- 10 Further examples of suitable surfactants are compounds commonly used as surface-active agents given in the well-known textbooks "Surface Active Agents" Vol.1, by

  Schwartz & Perry, Interscience 1949, Vol.2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of

  15 "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981.
- The product may additionally contain a disintegrant known in the art to aid disintegration and quick dissolution of the product in a bucket or bowl of water. Suitable examples thereof are Acusol 771 (TM of Rohm & Haas), Disintex 75 (TM of ISP) or combinations of a suitable acid (e.g. citric, fumaric, maleic or tartaric) and sodium bicarbonate. The product may also contain a salt which is able to take up any residual water as water of crystallisation (e.g. anhydrous sodium sulphate or sodium carbonate).

The core contents should not adversely interact with the shell 30 material because this could lead to a diminishing of the shell strength during storage. Thus, the core is substantially non-aqueous, which means that the water content of the core will be such that it does not dissolve, weaken or otherwise adversely

11

interact with the water soluble shell. Normally the total core contents will contain at most 15% by weight of water, preferably at most 10%, more preferably at most 5% or even 2%. This is in sharp contrast to normal liquid cleaning compositions, which usually contain large amounts of water, conventionally 50% or more.

Additionally, the core material compositions may comprise other benefit agents suitable for the intended end use of the unit dose cleaning product, such as: sequestrants, builders, bleaching agents, enzymes, pH buffers, skin care agents, dyes, perfume, etc.

As outlined above, the core material quickly and easily

15 dissolves in the intended amount of water. As some surfactants, when going from a highly concentrated state to a dilute aqueous solution, pass through a very viscous gel state in which further dissolution is slow, it is preferred either to chose surfactants or surfactant combinations with which this

20 phenomenon does occur not at all or only to a limited extent, or to add materials which prevent or diminish its occurrence, such as hydrotropes well known in the detergents art.

The unit dose cleaning products according to the invention may 25 be suitable for a variety of cleaning purposes, depending on the choice of the surfactants and optionally other benefit agents. Thus, they can be used e.g. for bath products for personal use or for pets or they can be used for cleaning of all kinds of hard or soft surfaces in and around the house.

30 Since the rigid and smooth appearance of the products give the consumer an impression of concentrated strength, they are particularly suitable for all kinds of hard surface cleaning jobs involving the removal of tough soil, such as fo hand or

12

machine dish washing and for kitchen, bathroom, toilet and floor cleaning.

Although the unit dose products may be prepared in any shape or 5 form, to be attractive to the consumer am object with a symmetrical shape is highly preferred and round shapes such as ovals (egg-like), lens-like shapes, balls or bullets are very suitable. Other suitable round forms are cylinders with an oval or circular cross section.

10

Even more preferred are unit dose objects which have a crystal-like shape, which for the purposes of this invention is defined as a shape completely defined by flat surfaces. Such objects are also known as polyhedrons. The most simple shape meeting this requirement is a three-sided pyramid. Other suitable forms are: 4-8 sided pyramids, bi-pyramids, rhombohedra, blocks, cubes and similar shapes. Representative shapes are shown in figures 1, 2 and 3.

20 The visual appearance of the unit dose products may be further improved and the appeal to the consumer increased by giving the core and the shell a different colour. Thus, the shell may be colourless or lightly coloured, whereas the core may have a bright contrasting colour.

25

The liquid core may further contain one or a plurality of solid particles or capsules of a size clearly visible to the naked eye and in an amount which does not interfere with the transparancy or translucency of the product. Generally these particles will make up less than 80% of the total core material, preferably less than 50%. The visibility of these particles or capsules may be further enhanced by giving them a colour which is different from that of the shell and/or the

liquid core. These particles and capsules may have the same composition as the remainder of the unit dose product or they may have a composition which is different from that of the liquid core. Thus, such particles or capsules are a suitable vehicle for adding components which are preferably kept separate from the components of the liquid core e.g. because of physical or chemical incompatibility between the components in the particles or capsules and those in the remainder of the liquid core.

10

The unit dose product may be produced by suitable methods known in the art. Particularly the art of candy making provides suitable examples of processes adaptable to the production of the unit dose products. For the homogeneous products suitable processes include mixing/melting all components together and simply casting the melt in dies, or processing the mixture by injection moulding using an extruder. For the products with a liquid core a suitable process involves processing of the shell material through an extruder fitted with a co-extrusion head through which the liquid core material and the shell material are injected simultaneously in a die.

## Examples

Shell material was prepared according to the formulae given in the table below:

5

Component (%)	1	2	3	4	5
					20.5
Sorbitol	57	57	60	70	39.5
Sodium Acetate	25	25			20
PEG 400 to 6000	10	10	10	10	
PVA		5	5		
PVP	5				
Glycerol/Tri-	3	3		3	
acetine					
Citric acid			10	10	
Sodium				7	
bicarbonate					
Soluble pre-			14.8		40
gelatinized					
starch					
Disintegration			0.2		0.5
Polymers					

The shell material and shell shape was prepared using one of the routes described below:

## 10 1) Wet preparation and extrusion:

An intimate mixture is prepared of all compatible ingredients by dissolving/slurrying them in water and spray drying the concentrated slurry under vacuum at 120-140°C. The incompatible ingredients are added thereafter. This mixture was extruded

15 through a co-extrusion head simultaneously with a coloured liquid detergent core material into rectangular dies producing blocks having a hard translucent shell through which the coloured liquid core was visible.

## 20 2) Dry preparation and extrusion:

All shell materials were intimately mixed in the dry state and extruded as above.

### 3) Molding of sheet material:

All shell ingredients were mixed and heated to 80-90°C with addition of about 20% water. After a homogeneous liquid was 5 obtained water was removed under vacuum at a temperature of between 130-150°C to a level of about 0.5% or less. The viscous liquid was poured on a flat surface and rolled to a flexible sheet of about 2mm thickness which was shaped into a multitude of hollow pyramids of the desired shape by pressing it into a 10 suitable mold. The pyramids were filled with the core material covered with a second sheet of the same (or different) shell material which was fixed to the pyramid walls, while still hot, by applying sufficient pressure on the sheet. The filled pyramids were cut out of the sheet and left to cool and age for 15 several hours during which the flexible walls became rigid while remaining transculent.

The liquid detergent core material consisted of the following ingredients:

20	Lorodac L6S50*	20.0%		
	Biodac 59**	50.0%		
	Fatty acid mixture	3.0%		
	Ethoxylated/propoxylated fatty amine			
	Perfume	5.0%		
25	Colour	minor		

- \*  $C_{12-15}$  fatty alcohol alkoxylated with (average) 5EO + 2PO, nonionic surfactant marketed by Condea Augusta.
- \*\*  $C_{10}$  alkohol ethoxylated with (average) 5 EO, nonionic 30 surfactant marketed by Condea Augusta.

16

#### Claims

 Unit dose cleaning product which is completely soluble in water and comprises a detergent surfactant characterized in that it is rigid, has a smooth surface and is at least partially transparent or translucent.

- 2. Cleaning product according to claims 1 characterized in that it cannot be squeezed by hand such that its dimensions in any one direction alter by more than 10% of the original value.
- 3. Cleaning product according to claims 1 and 2 characterized in that it consists of a solid homogeneous mixture comprising a structuring material and one or more detergents.
- 4. Cleaning product according to claims 1 and 2 characterized in that it has a rigid outer shell comprising a structuring material, surrounding a solid or liquid core comprising detergent surfactant.
- 5. Cleaning product according to claim 4 characterized in that the core comprises a liquid.
- 6. Cleaning product according to claims 1-5 characterized in that it completely dissolves in 5 minutes at 100°C in 2000 times its weight of water.
- 7. Cleaning product according to claim 6 characterized in that it completely dissolves in 2 minutes at 70°C in 1000 times its weight of water.

WO 01/85895

8. Cleaning product according to claims 1-7 characterized in that it has a symmetrical shape.

17

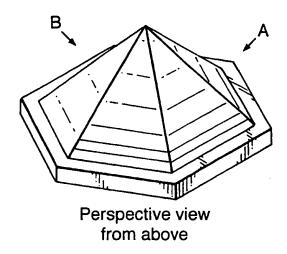
PCT/EP01/04937

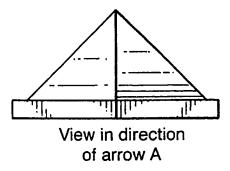
- •9. Cleaning product according to claim 8 characterised in that it has a round shape
- 10. Cleaning product according to claim 8 characterized in that it has a crystal-like shape.
- 11. Cleaning product according to claims 8-10 characterized in that the shell and the core have different colours.

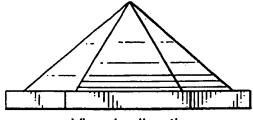
PCT/EP01/04937

1 / 3

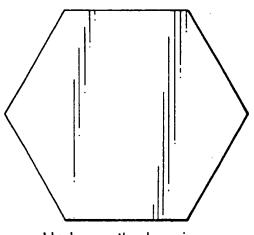
Figure 1





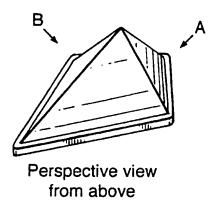


View in direction of arrow B

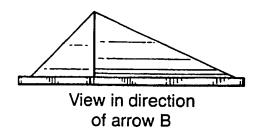


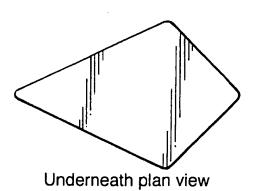
Underneath plan view

Figure 2.



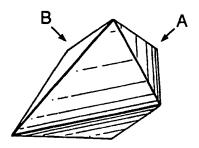
View in direction of arrow A



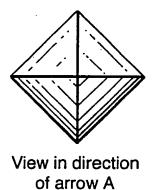


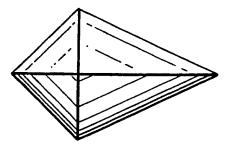
3 / 3

Figure 3

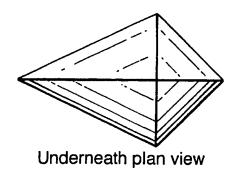


Perspective view from above





View in direction of arrow B



### INTERNATIONAL SEARCH REPORT

łn. ational Application No

PCT/EP 01/04937 A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C11D17/00 A61K A61K7/50 According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C11D A61K IPC 7 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. EP 0 266 796 A (SHOWA DENKO KK) X 1,2,4-911 May 1988 (1988-05-11) page 4 -page 5; claims; examples 6,7 EP 0 573 978 A (KAO CORP) X 1,2,4-10 15 December 1993 (1993-12-15) cited in the application page 4; claims page 9 examples X WO 96 24328 A (UNICHEMA CHEMIE BV) 1-9 15 August 1996 (1996-08-15) page 6; claims examples -/--Χİ Further documents are listed in the continuation of box C. Patent family members are listed in annex. Special categories of cited documents: \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance invention "E" earlier document but published on or after the international "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled \*O\* document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed \*&\* document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 23 July 2001 06/08/2001 Name and mailing address of the ISA Authorized officer European Palent Office, P.B. 5818 Patentlaan 2

1

NL - 2280 HV Rijswijk

Fax: (+31-70) 340-3016

Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,

Pfannenstein, H

## INTERNATIONAL SEARCH REPORT

im. .ational Application No PCT/EP 01/04937

Cataga	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Category *	Cuation of document, with makanon, where appropriate, or the relevant passages	nesevani io ciaim no.
х	US 3 705 102 A (MAST ROLF) 5 December 1972 (1972-12-05) cited in the application column 2; claims	1,2,4-10
<b>X</b>	EP 0 879 874 A (HENKEL KGAA) 25 November 1998 (1998–11–25) page 3 –page 4; claims	1,2,4-10
X	EP 0 339 707 A (UNILEVER PLC ;UNILEVER NV) 2 November 1989 (1989-11-02) page 3; claims	1,2,4-10
X	DATABASE WPI Section Ch, Week 199813 Derwent Publications Ltd., London, GB; Class D25, AN 1998-141276 XP002148580 & JP 10 017899 A (KAMITSUKI M), 20 January 1998 (1998-01-20) abstract	1
X	DATABASE WPI Section Ch, Week 198320 Derwent Publications Ltd., London, GB; Class D21, AN 1983-48259K XP002172732 & JP 58 061200 A (POLA KASEI KOGYO KK), 12 April 1983 (1983-04-12) abstract	1-4,8,9,

1

## INTERNATIONAL SEARCH REPORT

Information on patent family members

In. (ational Application No PCT/EP 01/04937

Patent document Publication Cited in search report date			Publication date		Patent family member(s)	Publication date	
EP	0266796	A	11-05-1988	DE	3778118 A	14-05-1992	
				JP	2562624 B	11-12-1996	
				JP	63252543 A	19-10-1988	
				US	4898781 A	06-02-1990	
ΕP	0573978	Α	15-12-1993	DE	69324523 D	27-05-1999	
				DE	69324523 T	09-09-1999	
				JP	2784872 B	06-08-1998	
				JP	6055060 A	01-03-1994	
				US	5385737 A	31-01-1995	
				JP	2961587 B	12-10-1999	
				JP	6079165 A	22-03-1994	
WO	9624328	Α	15-08-1996	AU	4789296 A	27-08-1996	
				BR	9607118 A	04-11-1997	
				CN	1173814 A	18-02-1998	
				EP	0808152 A	26-11-1997	
				JP	10513189 T	15-12-1998	
US	3705102	A	05-12-1972	NON			
EP	0879874	A	25-11-1998	DE	19721708 A	26-11-1998	
EP	0339707	Α	02-11-1989	CA	1336485 A	01-08-1995	
				DE	68919518 D	12-01-1995	
				JP	2016198 A	19-01-1990	
JP	10017899	Α	20-01-1998	NONE			
JP	58061200	A	12-04-1983	JP	1343490 C	29-10-1986	
				JP	61002720 B	27-01-1986	